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Electrical Properties of CuO-Doped PZT-PZN-PMnN Piezoelectric Ceramics Sintered at Low Temperature

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Abstract

The $0.8Pb(Zr_{0.48}Ti_{0.52})O_3$-$0.125Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.075Pb(Mn_{1/3}Nb_{2/3})O_3$ (PZT-PZN-PMnN) + x wt% CuO piezoelectric ceramics, where x = 0.0, 0.05, 0.075, 0.10, 0.125, 0.150, and 0.175, have been fabricated by the conventional solid-state reaction method and the B-site Oxide mixing technique (BO). The effect of CuO on the sinterability, structure, and electrical properties of PZT-PZN-PMnN ceramics was systematically studied. The CuO addition significantly reduced the sintering temperature of the ceramics from 1150˚C to 850˚C. Experimental results showed that with the doping of CuO, all the ceramics could be well sintered and exhibit a dense, pure perovskite structure. The specimen containing 0.125 wt% CuO sintered at 850˚C showed the good electrical properties: the density of 7.91 g/cm³; the electromechanical coupling factor, $k_p = 0.55$ and $k_t = 0.46$; the dielectric constant, $\varepsilon = 1179$; the dielectric loss ($\tan\delta$) of 0.006; the mechanical quality factor (Q_m) of 1174; the piezoelectric constant (d_{31}) of 112 pC/N.

Keywords

Crystal Structure, Dielectric, Piezoelectric Constant, Mechanical Quality Factor

1. Introduction

In recent years, many material scientists are interested in research and application of multi-component piezoelectric ceramics combine PZT with relaxor ferroelectrics, such as $Pb(Zr_{0.48}Ti_{0.52})O_3$-$Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZT-PZN), $Pb(Zr_{0.48}Ti_{0.52})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PZT-PMN), $Pb(Zr_{0.48}Ti_{0.52})O_3$-$Pb(Zn_{1/3}Nb_{2/3})O_3$-$Pb(Mn_{1/3}Nb_{2/3})O_3$

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(PZT-PZN-PMnN), etc., due to their excellent piezoelectric properties and many applications in piezoelectric actuators and transformers [1]-[6]. These ceramics often have large dielectric constant ε, high mechanical quality factor (Q_m), high electromechanical coupling factor (k_p), high Curie temperature and low dielectric loss factor ($\tan\delta$). However, the sintering temperature of the ceramics is quite high (>1150˚C), which leads evaporation of PbO during sintering process, resulting in reducing properties of ceramic compositions and environmental pollution. Therefore, lowering sintering temperature of PZT based ceramics is very necessary.

There are many methods to lower the sintering temperature, however, the most common and effective method to reduce the sintering temperature of PZT based ceramics is to add the low-temperature melting oxides or compounds for liquid phase sintering at a low temperature. Many researchers have successfully decreased the sintering temperature of PZT based ceramics by using various additives such as B_2O_3, Bi_2O_3, Li_2CO_3, $BiFeO_3$, CuO, CuO + Bi_2O_3, etc. [7]-[14].

In some cases, these additives can facilitate lower the sintering temperature, but decrease simultaneously the piezoelectric properties of ceramics due to the formation of piezoelectrically inactive phases in the grain boundary regions. Therefore, the research and fabrication ceramics sintered at low temperature, while improving or not reducing the piezoelectric properties of ceramics system are very important.

Recently, we studied the effect of Li_2CO_3 addition on the sintering behaviour and physical properties of PZT-PZN-PMnN ceramics. We decreased the sintering temperature of ceramics from 1150˚C to 930˚C and maintained good electrical properties: the electromechanical coupling factor k_p = 0.64, the dielectric constant ε = 1320, the dielectric loss ($\tan\delta$) of 0.005, the mechanical quality factor (Q_m) of 1150, the piezoelectric constant (d_{31}) of 145 pC/N, and the remanent polarization (P_r) of 30.5 µC/cm^2 [7].

In this work, we present some research results on the effect of CuO on the sinterability, structure, and electrical properties of PZT-PZN-PMnN ceramics.

2. Experimental Procedure

The general formula of the studied material was $0.8Pb(Zr_{0.48}Ti_{0.52})O_3$-$0.125Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.075Pb(Mn_{1/3}Nb_{2/3})O_3$ (PZT-PZN-PMnN) + x wt% CuO, where x = 0.0, 0.05, 0.075, 0.10, 0.125, 0.150, and 0.175. Reagent grade oxide powders of PbO, ZnO, MnO_2, Nb_2O_5, ZrO_2, TiO_2 and CuO (purity ≥ 99%) were used as starting materials.

The PZN based ceramic materials with the a pure perovskite structure are very difficult to prepare by conventional ceramic processing, because of the high polarizability of Pb^{2+} and its interaction with Zn^{2+} cations, resulting the formation of the pyrochore phase and they will be detrimental to the physical properties of lead based ferroelectric ceramics [15]. Therefore, in this work, we combined the conventional solid-state reaction method and the B-site Oxide mixing technique (BO) for fabricate ceramic samples. Firstly, the mixture of $(Zn_{0.125}Mn_{0.075})Nb_{0.4}[(Zr_{0.48}Ti_{0.52})_{2.4}]O_6$ (BO) were prepared by reactions of ZnO, MnO_2, Nb_2O_5, ZrO_2 and TiO_2 at temperature 1100˚C for 2 h. Then, the powders of BO and PbO were weighed and milled for 8 h. The powders were calcined at temperature 850˚C for 2 h, producing the PZT-PZN-PMnN compound. Thereafter CuO were mixed with the calcined PZT-PZN-PMnN powder, and powders milled for 16 h. The ground materials were pressed into disk 12 mm in diameter and 1.5 mm in thick under 100 MPa. These pellets were coated with $PbZrO_3$ powder then were sintered in a sealed alumina crucible at the temperature of 800˚C, 830˚C, 850˚C, and 870˚C for 4 h.

The crystal structure of the sintered samples was examined by X-ray diffraction (XRD, D8 ADVANCE). The microstructure of the samples was examined by using a scanning electron microscope (SEM) (Hitachi S-4800). The densities of samples were measured by Archimedes method. The ceramic samples were polled in a silicone oil bath at 120˚C by applying dc field of 30 kV/cm for 20 min then cooling down to room temperature under the same electric field. They were aged for 24 h prior to testing. The piezoelectric properties were determined by the resonance and antiresonance frequencies using an impedance analyzer (HP 4193A and RLC HIOKI 3532). Temperature dependence of dielectric constant was determined using RLC HIOKI 3532 with automatic programming; temperature of the samples was measured using Digital Multimeter 7562. The ferroelectric property was measured by Sawyer-Tower method.

3. Results and Discussion

Figure 1 shows the densities as a function of sintering temperature for PZT-PZN-PMnN ceramics with various

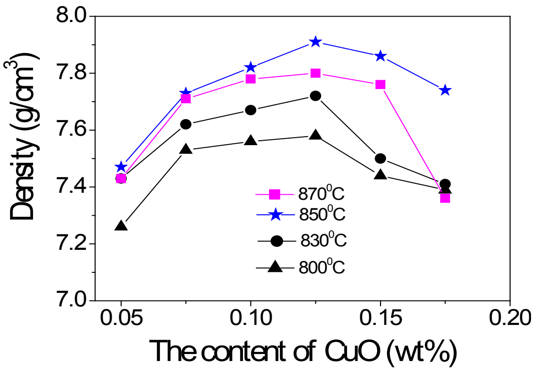

Figure 1. The density of PZT-PZN-PMnN ceramics with different amounts of CuO additive sintered at different temperatures: 800˚C, 830˚C, 850˚C, and 870˚C.

CuO additions. With increasing of sintering temperature and CuO content, the density increases and reaches the maximum value (7.91 g/cm^3) at 850˚C sintering temperature and at 0.125 wt% CuO content, then decreases. In our previous work [7], the sintering temperature of undoped PZT-PZN-PMnN ceramics was as high as 1150˚C (the density of 7.82 g/cm^3). Thus, the addition of CuO improved the sinterability, reduced the sintering temperature of 300˚C compared with pure samples and increasing density of the ceramic samples. The above results consistent with the work of the authors Kim and co-worker studied the effect of CuO on structure and electrical properties of 0.4 $Pb(Mg_{1/3}Nb_{2/3})O_3$-0.25$PbZrO_3$-0.35$PbTiO_3$ ceramic system [16].

Figure 2 shows the SEM images of the PZT-PZN-PMnN + x wt% CuO ceramics sintered at 850˚C: (a) x = 0.0, (b) x = 0.05, (c) x = 0.075, (d) x = 0.10, (e) x = 0.125 and (g) x = 0.150. **Figure 2(a)** shows the microstructure of discrete grains, porous, not sintered materials. However, the microstructure of samples becomes denser and grain size increases as the CuO sintering aid is increased (**Figures 2(b)-(e)**). A homogeneous microstructure developed for the sample with 0.125 wt% CuO added (**Figure 2(e)**). However, **Figure 2(g)** also shows that further increasing the CuO content to 0.125 wt% gives rise to an abnormal grain boundary, porous appeared, the average grain size reduces. Such with the 0.125 wt% CuO-added sample, the highly dense and homogeneous microstructure was obtained, which may expect improved properties of ceramics.

The lowering of the sintering temperature and grain growth with CuO addition can be explained by liquid phase sintering. The phase diagram of Hitoshi Kitaguchi [17] has shown that CuO and PbO form the liquid phase at point eutectic 789˚C. So when CuO doped in PZT-PZN-PMnN ceramics, CuO reacted with PbO and formed a liquid phase during the sintering, which assisted the densification of the specimens and increasing grain size. The second phase occurs at grain boundaries related to the limited solubility of CuO.

Figure 3 shows the XRD patterns of the PZT-PZN-PMnN + x wt% CuO ceramic samples sintered at 850˚C for 4 h. It can be seen that all samples exhibit a perovskite structure, and not detect a second phase until x = 0.125. However, when the CuO content increases over 0.125 wt%, second phase peak was observed. Crystal structure of the samples is modified significantly by CuO additions. For the pure sample (x = 0.0), the rhombohedral structure developed. All the samples with the addition of CuO had a tetragonal structure as indicated by the splitting of (002) and (200) peaks at $2\theta \approx 44˚$. However, phase transition did not appear. This result suggests that Cu^{2+} ions are substituted for B-site of perovskite structure ABO_3 which lead to the distortion of crystal lattice. The results are consistent with several published works [18]-[21].

Figure 4 shows temperature dependence of dielectric constant ε and dielectric loss tanδ as a function of CuO content. With increasing CuO doping, Curie temperature (T_c) of PZT-PZN-PMnN ceramics slight decreases. The composition with 0.125 wt% CuO content shows highest peak dielectric constants (12,000), which appears at about 266˚C.

Figure 5 shows temperature dependence of dielectric constant ε of 0.125 wt% CuO-doped ceramic sample measured at frequency of 1 kHz, 10 kHz, 100 kHz and 1 MHz. It can be seen that the shape of the ε (T) peaks are broad, which is typical of a case diffuse transition with frequency dispersion. When the measured frequency increases, the maximum of ε_{max} decreases and shifts toward higher temperatures while dielectric loss increases near the Curie point, which is typical of a relaxor material [1] [7].

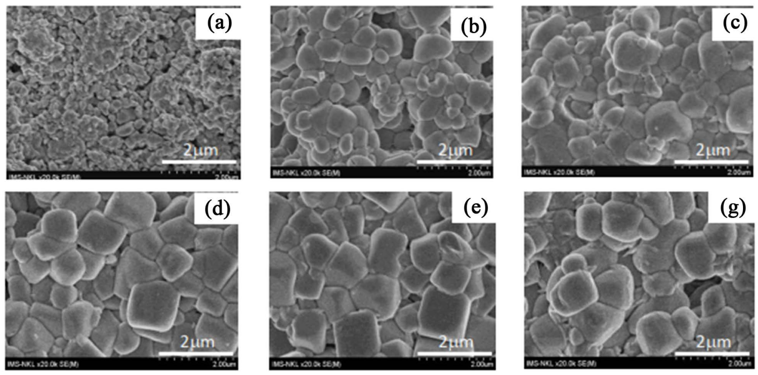

Figure 2. SEM images of PZT-PZN-PMnN with different amounts of CuO additive sintered at 850˚C: (a) x = 0.0; (b) x = 0.05; (c) x= 0.075; (d) x = 0.10; (e) x = 0.125; (g) x = 0.150.

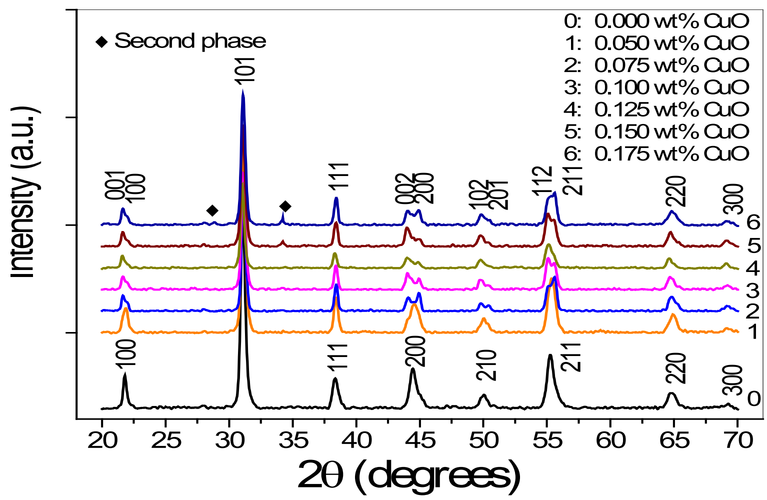

Figure 3. X-ray diffraction patterns of the PZT-PZN-PMnN with different amounts of CuO additive sintered at 850˚C: (0) x = 0.0; (1) x = 0.05; (2) x= 0.075; (3) x = 0.10; (4) x = 0.125; (5) x = 0.150; (6) x = 0.175.

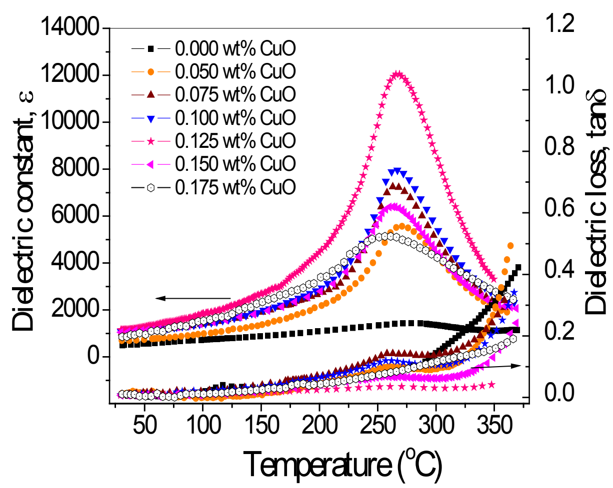

Figure 4. Temperature dependence of dielectric constant *ε* and dielectric loss tanδ of the PZT-PZN-PMnN ceramics with different amounts of CuO additive sintered at 850˚C.

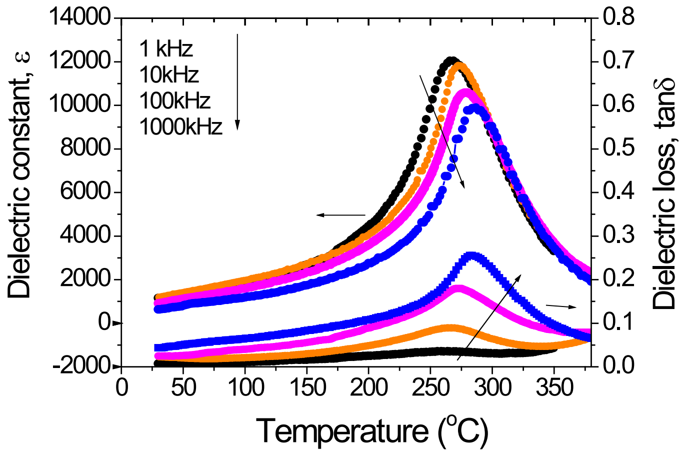

Figure 5. Temperature dependence of dielectric constant ε of 0.125 wt% CuO-doped sample measured at different frequencies: 1 kHz, 10 kHz, 100 kHz and 1 MHz.

To determine piezoelectric properties of ceramics, resonant vibration spectra of samples were measured at room temperature (**Figure 6**). From these resonant spectra, piezoelectric parameters of samples were determined.

Figure 7 and **Figure 8** show the electromechanical coupling factor (k_p, k_t), the piezoelectric constant (d_{31}), the mechanical quality factor (Q_m), the dielectric constant (ε) and dielectric loss (tanδ) change as a function of the CuO content. When the CuO content is lower than 0.125 wt%, the values of k_p, k_t, d_{31}, ε and Q_m are rapidly increase with increasing content of CuO, while the dielectric loss tanδ are strong decrease. The largest values for k_p of 0.55, k_t of 0.46, d_{31} of 112 pC/N, ε of 1179, Q_m of 1174 and minimum value of the dielectric loss tanδ is 0.006 were obtained at x = 0.125. These are probably related to characteristics of the density and the increasing grain size. During sintering, the presence of liquid phase enhances the density and grain size, which leads to the decrease of the energy loss and improvement of the electrical properties. Chao *et al*. [21] investigated CuO-doped PZT-PMN-PZN ceramics with compositions close to the morphotropic phase boundary (MPB) sintered at 920˚C. The optimized results of k_p (0.53), ε (982) and Q_m (1645) were obtained at 0.2 wt% CuO.

Nam *et al*. [14] also showed that CuO could increase the piezoelectric properties and reducing the sintering temperature of MnO_2-doped $0.75Pb(Zr_{0.47}Ti_{0.53})O_3$-$0.25Pb(Zn_{1/3}Nb_{2/3})O_3$ ceramics from 930˚C down to 850˚C The optimized values for k_p of 0.50, Q_m of 1000 were obtained at at 0.5 wt% CuO. The ceramic samples have a lower k_p and Q_m values than that of our ceramic samples. Accordingly, compared with the research results of F. Gao and co-workers on the PZT-PZN-PMnN ceramics [3], in our work with a small amount of CuO was added to PZT-PZN-PMnN ceramics reduced the sintering temperature of 300˚C, with the retention of good piezoelectric properties.

Figure 9 shows the shape of feroelectric hysteresis loops of the samples PZT-PZN-PMnN + x wt% CuO measured at room temperature. From the shape of these loops, the remanent polarization (P_r) and the coercive field (E_C) were determined, as shown in **Figure 10**. With increasing of CuO content, a sharp increases in P_r was observed for samples until x = 0.125, reaches the highest value (16 µC/cm^2) at x = 0.125, and then decreases, while the coercive field E_C strong decreases and reaches smallest value (4.5kV/cm) at x = 0.125. These results are in good agreement with the studied dielectric and piezoelectric properties of the ceramic samples.

4. Conclusion

The effect of CuO addition on the sintering behavior and physical properties of $0.8Pb(Zr_{0.48}Ti_{0.52})O_3$-$0.125Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.075Pb(Mn_{1/3}Nb_{2/3})O_3$ + x wt% CuO (x = 0.0 ÷ 0.175) ceramics was investigated. The addition of CuO improved the sinterability of the samples and caused an increase in the density and grain size at low sintering temperature (850˚C). All samples have pure perovskite phase. Crystal structure of the ceramics is modified significantly from rhombohedral structure to tetragonal structure by CuO additions. At the CuO content of 0.125 wt%, physical properties of ceramics are best: the density of 7.91 g/cm^3; the electromechanical

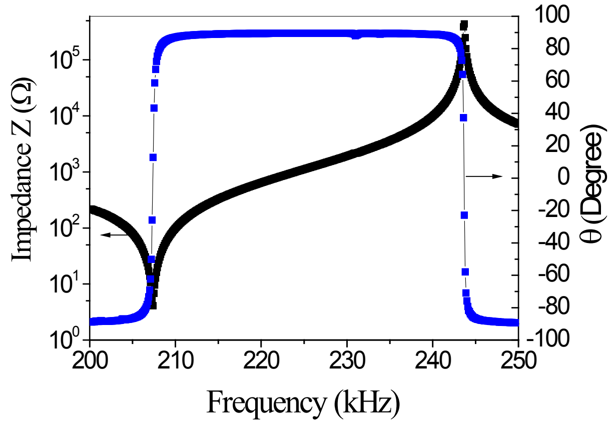

Figure 6. Spectrum of radial resonance of PZT-PZN-PMnN + 0.125 wt% CuO ceramic sample sintered at 850˚C.

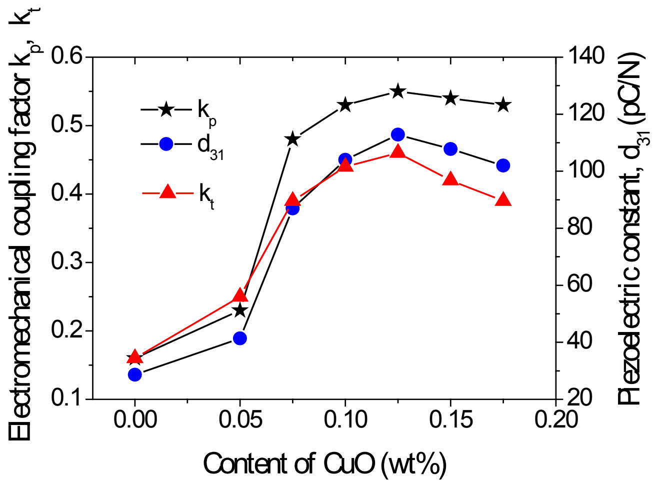

Figure 7. Electromechanical coupling factor k_p, k_t and piezoelectric constant d_{31} of PZT-PZN-PMnN ceramics sintered at 850˚C as a function of CuO content.

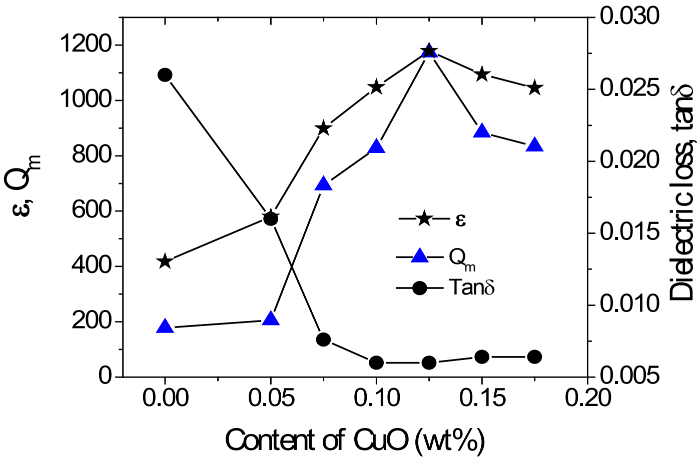

Figure 8. Dielectric constant ε, dielectric loss tanδ and mechanical quality factor Q_m of PZT-PZN-PMnN ceramics sintered at 850˚C as a function of CuO content.

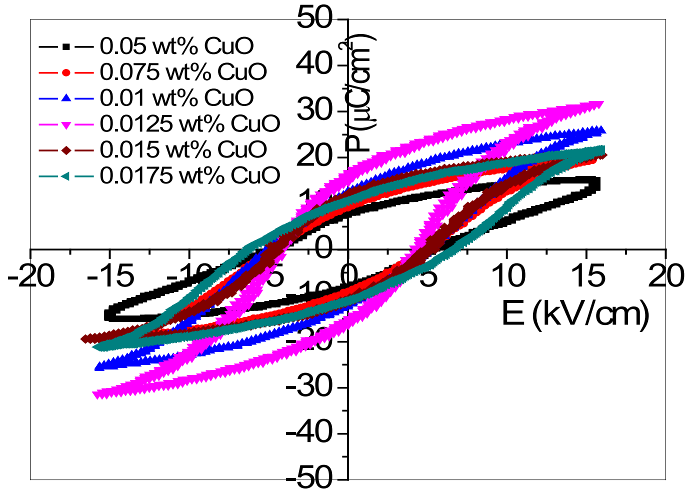

Figure 9. Hysteresis loops of PZT-PZN-PMnN + x wt% CuO ceramic samples.

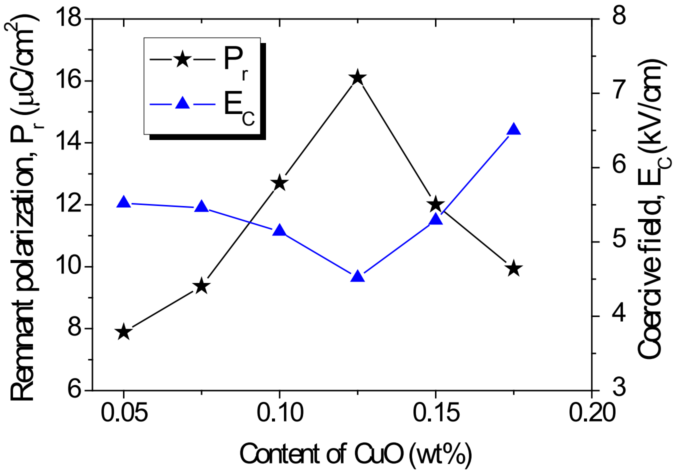

Figure 10. The remnant polarization (P_r) and coercive field (E_C) as a function of the CuO content.

coupling factor, $k_p = 0.55$ and $k_t = 0.46$; the dielectric constant, $\varepsilon = 1179$; the dielectric loss ($\tan\delta$) of 0.006; the mechanical quality factor (Q_m) of 1174; the piezoelectric constant (d_{31}) of 112 pC/N; the remanent polarization (P_r) of 16 μC/cm^2. The improvement of the electrical properties of the ceramics after adding CuO is mainly due to the presence of liquid phase in during sintering enhances the density and grain size, which leads to the decrease of the energy loss and improvement of the electrical properties.

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